

Solid C_{60} : a new form of carbon

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A new form of pure, solid carbon has been synthesized consisting of a somewhat disordered hexagonal close packing of soccer-ball-shaped C_{60} molecules. Infrared spectra and X-ray diffraction studies of the molecular packing confirm that the molecules have the anticipated 'fullerene' structure. Mass spectroscopy shows that the C_{70} molecule is present at levels of a few per cent. The solid-state and molecular properties of C_{60} and its possible role in interstellar space can now be studied in detail.

FOLLOWING the observation that even-numbered clusters of carbon atoms in the range C_{30} – C_{100} are present in carbon vapour¹, conditions were found^{2–4} for which the C_{60} molecule could be made dominant in the large-mass fraction of vapourized graphite. To explain the stability of the molecule, a model was proposed of an elegant structure in which the carbon atoms are arranged at the 60 vertices of a truncated icosahedron, typified by a soccer ball. The structure, dubbed buckminsterfullerene² because of its geodesic nature, has been the subject of several theoretical stability tests^{5,6} and has been discussed widely in the literature. Calculations of many physical properties have been made, including electron energies^{7–9}, the optical spectrum⁹, vibrational modes^{10–15}, and the electric and magnetic properties^{16,17}. There has been speculation on the possible chemical and industrial uses of C_{60} (ref. 2), and on its importance in astrophysical environments^{18–20}. Until now, it has not been possible to produce sufficient quantities of the material to permit measurement of the physical properties, to test the theoretical calculations, or to evaluate the possible applications.

Some of us have recently reported evidence^{21,22} for the presence of the C_{60} molecule in soot condensed from evaporated graphite. The identification was based primarily on the observed isotope shifts of the infrared absorptions when ^{12}C was replaced by ^{13}C , and on comparison of the observed features with theoretical predictions. The measured infrared and ultraviolet absorption bands were superimposed on a rather large continuum background absorption from the graphitic carbon which comprised $\geq 95\%$ of the sample. Here we report how to extract the carrier of the features from the soot, how to purify it, and evidence that the material obtained is in fact primarily C_{60} .

Method of production

The starting material for our process is pure graphitic carbon soot (referred to below as simply soot) with a few per cent by weight of C_{60} molecules, as described in refs 21, 22. It is produced by evaporating graphite electrodes in an atmosphere of ~ 100 torr of helium. The resulting black soot is gently scraped from the collecting surfaces inside the evaporation chamber and dispersed in benzene. The material giving rise to the spectral features attributed to C_{60} dissolves to produce a wine-red to brown liquid, depending on the concentration. The liquid is then separated from the soot and dried using gentle heat, leaving a residue of dark brown to black crystalline material. Other non-polar solvents, such as carbon disulphide and carbon tetra-

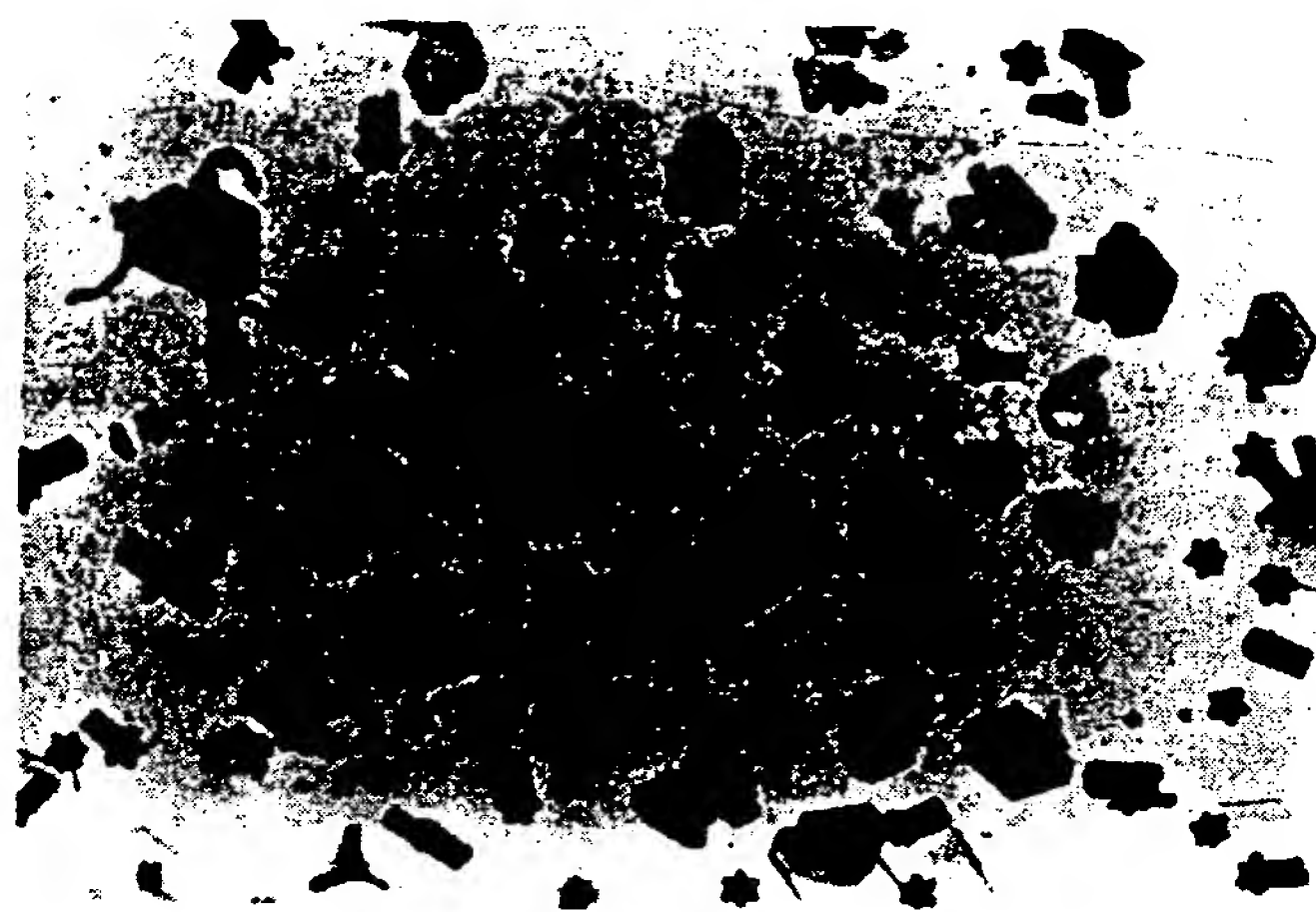


FIG. 1 Transmission micrograph of typical crystals of the C_{60} showing thin platelets, rods and stars of hexagonal symmetry.

centration procedure is to heat the soot to $400^\circ C$ in a vacuum or in an inert atmosphere, thus subliming the C_{60} out of the soot (W. Schmidt, personal communication). The sublimed coatings are brown to grey, depending on the thickness. The refractive index in the near-infrared and visible is about two. To purify the material, we recommend removing the ubiquitous hydrocarbons before the concentration procedure is applied (for example, by washing the initial soot with ether). Thin films and powder samples of the new material can be handled without special precautions and seem to be stable in air for at least several weeks, although there does seem to be some deterioration with time for reasons that are as yet unclear. The material can be sublimed repeatedly without decomposition. Using the apparatus described, one person can produce of the order of 100 mg of the purified material in a day.

Studies by optical microscopy of the material left after evaporating the benzene show a variety of what appear to be crystals—mainly rods, platelets and star-like flakes. Figure 1 shows a micrograph of such an assemblage. All crystals tend to exhibit six-fold symmetry. In transmitted light they appear red to brown in colour; in reflected light the larger crystals have a metallic appearance whereas the platelets show interference colours. The platelets can be rather thin and are thus ideally suited for electron-diffraction studies in an electron microscope (see the inset in Fig. 3).

Mass spectroscopy

The material has been analysed by mass spectrometry at several facilities. All mass spectra have a strong peak at mass 720 a.m.u., the mass of C_{60} . Significant differences in the spectra occur only at masses lower than 300 a.m.u. Most of these differences seem to originate from the different ionization techniques and in the different methods of desorbing molecules from the sample. Mass spectra recorded at low and high resolution are shown in Fig. 2. The spectra were obtained using a time-of-flight secondary-ion mass spectrometer²³ and a C_{60} -coated stainless-steel plate. In the mass range above 300 a.m.u., the spectrum is dominated by C_{60} ions and its fragments (even-numbered clusters of atomic

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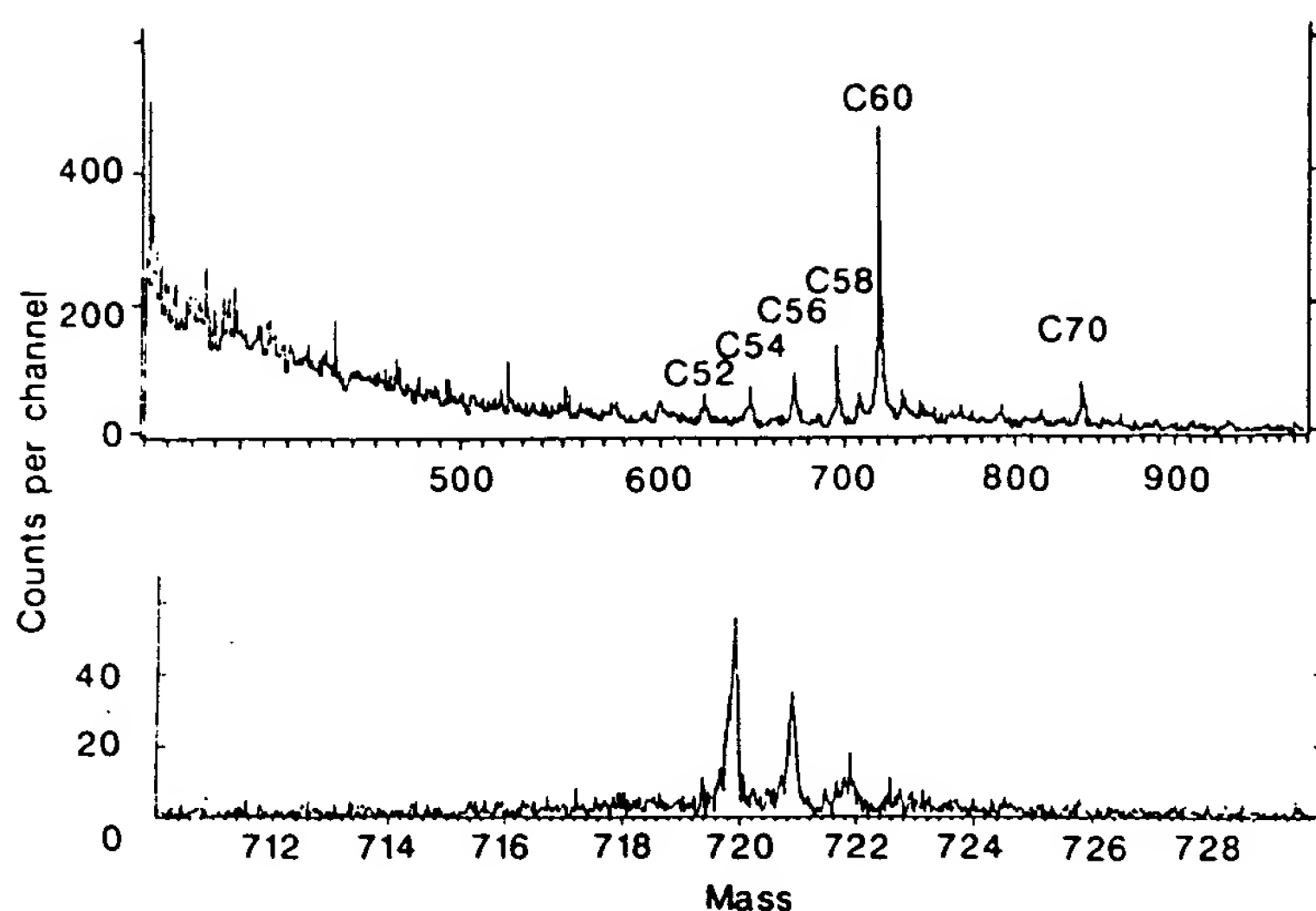


FIG. 2 Low-resolution (top) and high-resolution time-of-flight mass spectra of positive ions obtained from coatings of solid C_{60} . A 5-keV Ar^+ ion beam was used to sputter and ionize the sample. The isotope pattern (bottom) is approximately that expected for C_{60} molecules composed of ^{12}C and ^{13}C isotopes of natural abundance.

~ 0.1 . The high-resolution mass spectrum shows approximately the expected isotope pattern for C_{60} . The increasing background in the low-resolution mass spectrum is not produced by the sample—such backgrounds also occur in blank measurements on uncoated stainless-steel substrates.

So far, the cleanest mass spectra have been obtained when the material was evaporated and ionized in the vapour phase by electrons. In such spectra the low-mass background is substantially reduced and the entire mass spectrum is dominated by C_{60} ions and its fragments. The ratio of C_{70} to C_{60} in these mass spectra is ~ 0.02 and seems to be smaller than that shown in Fig. 2. Both ratios are of the order of those reported from laser-evaporation experiments^{2,3}. We assume, as previously suggested²⁴, that the C_{70} molecule also has a closed-cage structure, either elongated²⁴ or nearly spherical²⁵. Further details of the mass spectroscopy of the new material will be published elsewhere.

Structure

To determine if the C_{60} molecules form a regular lattice, we performed electron and X-ray diffraction studies on the individual crystals and on the powder. A typical X-ray diffraction pattern of the C_{60} powder is shown in Fig. 3. To aid in comparing the electron diffraction results with the X-ray results we have inset the electron diffraction pattern in Fig. 3. From the hexagonal array of diffraction spots indexed as shown in the figure, a d spacing of 8.7 Å was deduced corresponding to the (100) reciprocal lattice vector of a hexagonal lattice. The

most obvious correspondence between the two types of diffraction is between the peak at 5.01 Å of the X-ray pattern and the (110) spot of the electron diffraction pattern, which gives a spacing of ~ 5.0 Å. Assuming that the C_{60} molecules are behaving approximately as spheres stacked in a hexagonal close-packed lattice with a c/a ratio of 1.633, d spacings can be calculated. The results are shown in Table 1. The values derived from this interpretation are $a = 10.02$ Å and $c = 16.36$ Å. The nearest-neighbour distance is thus 10.02 Å. For such a crystal structure the density is calculated to be 1.678 g cm^{-3} , which is consistent with the value of $1.65 \pm 0.05 \text{ g cm}^{-3}$ determined by suspending crystal samples in aqueous $GaCl_3$ solutions of known densities. Although the agreement shown in Table 1 is good, the absence of the characteristically strong (101) diffraction of the hexagonal close-packed structure, and the broad continuum in certain regions suggest that the order is less than perfect. Further, X-ray diffraction patterns from carefully grown crystals up to 500 μm in size with well developed faces yielded no clear spot pattern (in contrast to the electron diffraction pattern on micrometre-sized crystals). It therefore appears that these larger crystals do not exhibit long-range periodicity in all directions.

A likely explanation for these facts lies in the disordered stacking of the molecules in planes normal to the c axis. It is well known that the positions taken by spheres in the third layer of stacking determines which of the close-packed structures occurs, the stacking arrangement in a face-centred cubic structure being ABCABC... whereas that in a hexagonal close-

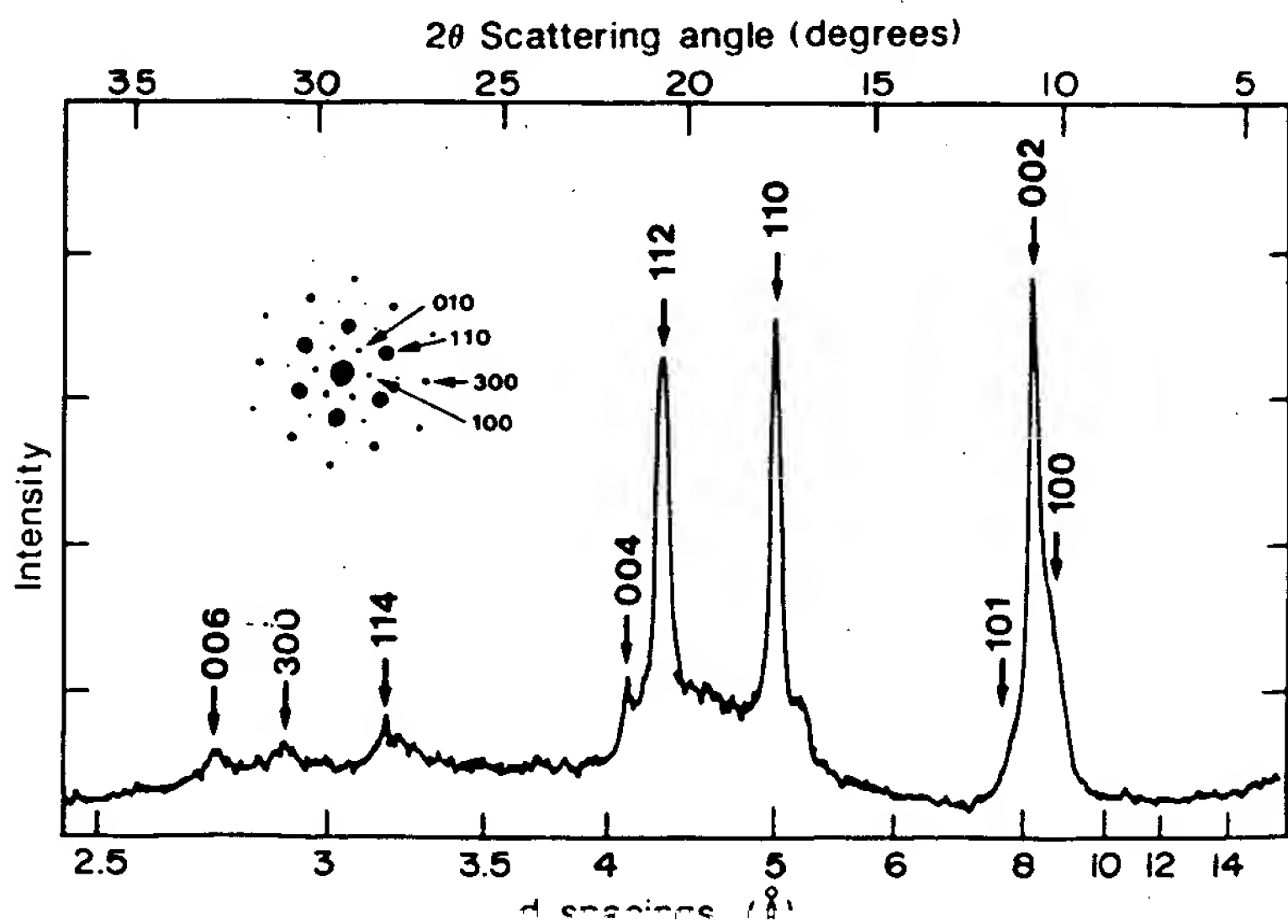


FIG. 3 X-ray diffraction pattern of a microcrystalline powder of C_{60} . Inset (upper left) is a single-crystal electron diffraction pattern indexed with Miller indices compatible with the X-ray pattern. The pattern is from a thin platelet such as those in Fig. 1 with the electron beam perpendicular to the flat face.

TABLE 1 X-ray diffraction results

Measured 2θ (deg)	Measured d spacing (Å)	Calculated d spacing (Å)	Assignment (hkl)
10.2 shoulder	8.7	8.68	(100)
10.81	8.18	8.18	(002)
		7.68	(101)
17.69	5.01	5.01	(110)
20.73	4.28	4.28	(112)
21.63	4.11	4.09	(004)
28.1	3.18	3.17	(114)
30.8	2.90	2.90	(300)
32.7	2.74	2.73	(006)

Assignments for a hexagonal lattice using $a=10.02$ Å, $c=16.36$ Å.
 $(1/d^2) = \frac{4}{3} [(h^2 + hk + k^2)/a^2] + l^2/c^2$.

packed structure is ABABAB... If the stacking sequence varies, the X-ray lines owing to certain planes will be broadened by the disorder whereas other lines will remain sharp. Such disordered crystalline behaviour was observed long ago in the hexagonal close-packed structure of cobalt²⁶⁻²⁸ where X-ray diffraction lines such as (101), (102) and (202) were found to be substantially broadened by the stacking disorder. Reflections from planes such as (002) remain sharp because these planes have identical spacings in the face-centred cubic and hexagonal close-packed structures. For the planes producing broadened diffraction peaks because of this kind of disorder, the following condition for the Miller indices (hkl) has been shown to apply^{27,29}: $h - k = 3l \pm 1$ (where l is an integer) and $l \neq 0$. None of these broadened reflections are apparent in the X-ray pattern of Fig. 3. This may explain the weakness of the characteristically strong (101) peak. Whether or not this stacking disorder is related to the presence of the possibly elongated C_{70} molecule has yet to be determined.

In small crystals at least, the C_{60} molecules seem to assemble themselves into a somewhat ordered array as if they are effectively spherical, which is entirely consistent with the hypothesis that they are shaped like soccer balls. The excess between the nearest-neighbour distance (10.02 Å) and the diameter calculated for the carbon cage itself (7.1 Å) must represent the effective van der Waals diameter set by the repulsion of the π electron clouds extending outward from each carbon atom. Because the van der Waals diameter of carbon is usually considered to be 3.3–3.4 Å the packing seems a little tighter than one might expect for soccer-ball-shaped C_{60} molecules. The reason for this has not yet been determined.

In summary, our diffraction data imply that the substance isolated is at least partially crystalline. The inferred lattice constants, when interpreted in terms of close-packed icosahedral C_{60} , yield a density consistent with the measured value. Further evidence that the molecules are indeed buckminsterfullerene and that the solid primarily consists of these molecules comes from the spectroscopic results.

Spectroscopy

The absorption spectra of the graphitic soot^{21,22} showed evidence for the presence of C_{60} in macroscopic quantities. Following the purification steps described above the material can be studied spectroscopically with the assurance that the spectra are dominated by C_{60} , with some possible effects from C_{70} . Samples were prepared for spectroscopy by subliming pure material onto transparent substrates for transmission measurements. Depending on the pressure of helium in the sublimation chamber, the nature of the coatings can range from uniform films (at high vacuum) to coatings of C_{60} smoke (sub-micrometre microcrystalline particles of solid C_{60}) with the particle size depending to some extent on the pressure.

Figure 4 shows the transmission spectrum of an ~ 2 - μ m-thick C_{60} coating on a silicon substrate. The infrared bands are at the same positions as previously reported^{21,22} with the exception

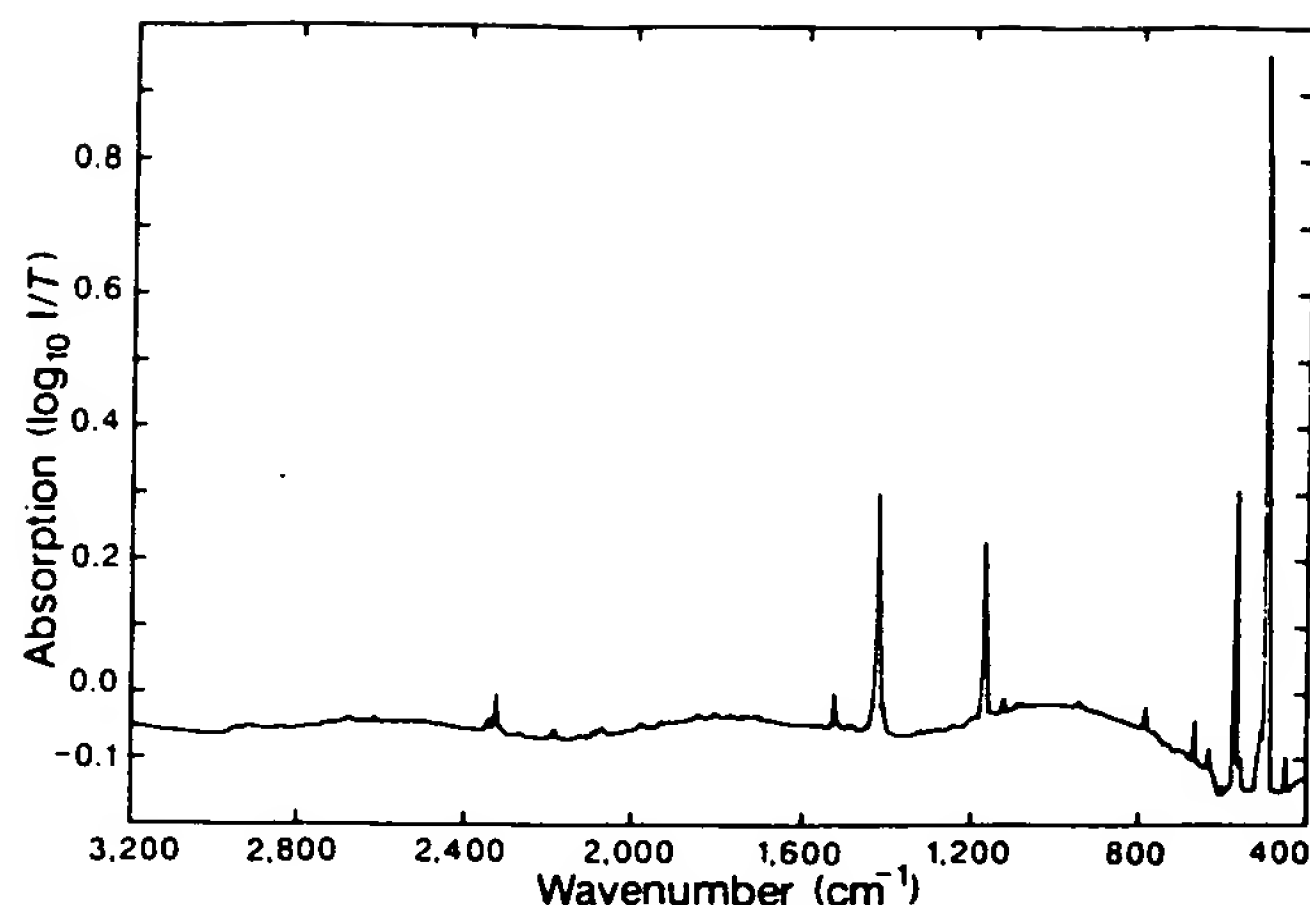


FIG. 4 Infrared absorption spectrum of a coating, ~ 2 μ m thick, of solid C_{60} on a silicon substrate, referenced to a clean silicon substrate. Apparent negative absorptions are due to the coating acting in part as a non-reflecting layer.

intense lines at 1,429, 1,183, 577 and 528 cm^{-1} ; here, however, there is no underlying continuum remaining from the soot. In many of our early attempts to obtain pure C_{60} , there was a strong band in the vicinity of 3.0 μ m, which is characteristic of a CH-stretching mode. After much effort this contaminant was successfully removed by washing the soot with ether and using distilled benzene in the extraction. The spectrum in Fig. 4 was obtained when the material cleaned in such a manner was sublimed under vacuum onto the substrate. The spectrum shows very little indication of CH impurities. Vibrational modes to compare with the measured positions of the four strong bands have been calculated by several workers¹⁰⁻¹⁵. As noted previously, the presence of only four strong bands is expected for the free, truncated icosahedral molecule with its unusually high symmetry. Also present are a number of other weak infrared lines which may be due to other causes, among which may be absorption by the C_{70} molecule or symmetry-breaking produced (for example) by isotopes other than ^{12}C in the C_{60} molecule or by mutual interaction of the C_{60} molecules in the solid. Weaker features at $\sim 2,330$ and $2,190$ cm^{-1} , located in the vicinity of the free CO_2 and CO stretching modes, may imply some attachment of the CO_2 or CO to a small fraction of the total number of C_{60} molecules. Another notable feature is the peak at 675 cm^{-1} , which is weak in the thin-film substrates but almost as strong as the four main features in the crystals. We suspect that this vibrational mode may be of solid state rather than molecular origin.

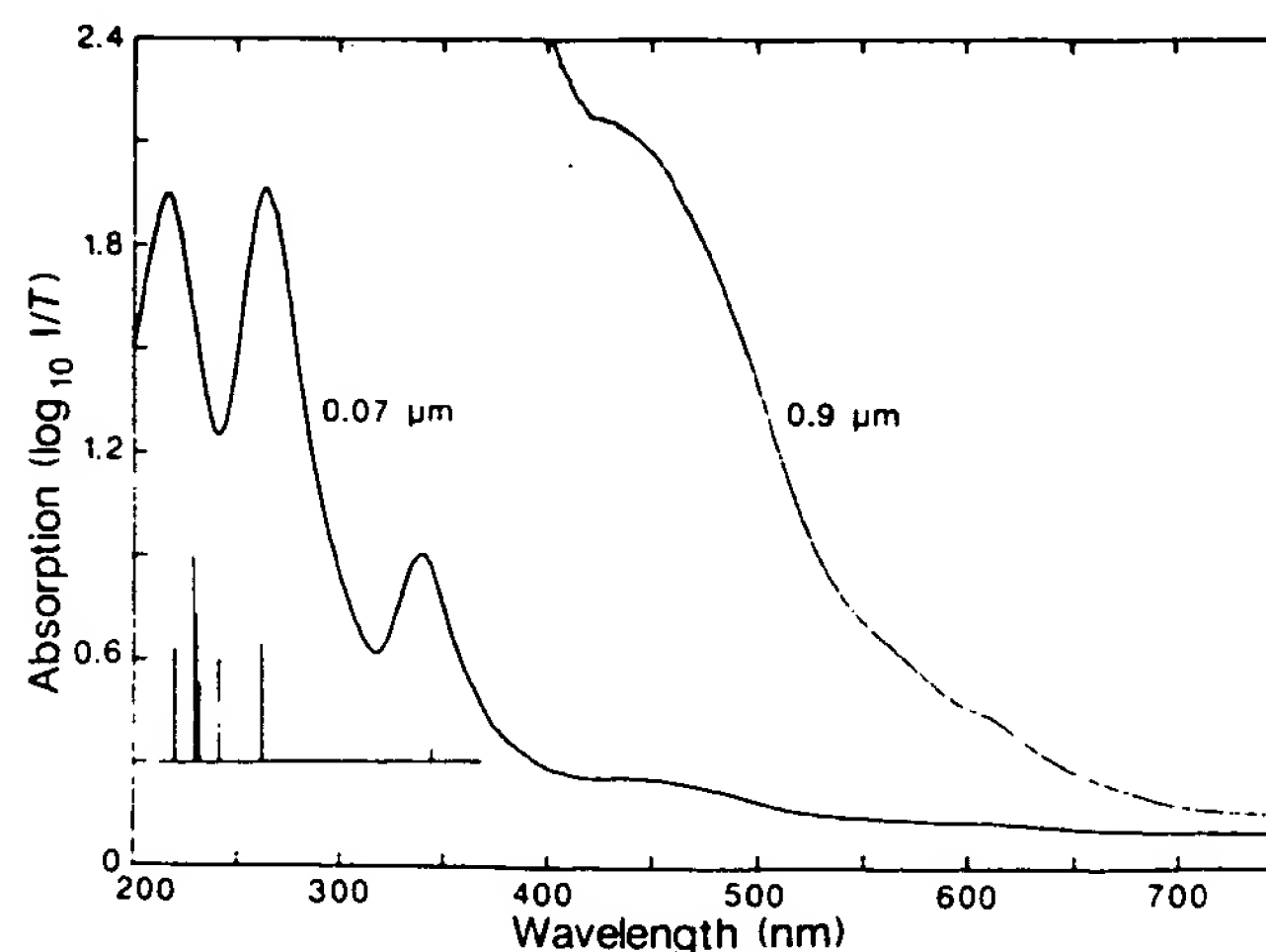


FIG. 5 Visible-ultraviolet absorption spectra of two thicknesses of solid C_{60} on quartz. The calculated⁹ positions and relative oscillator strengths for

Figure 5 shows an absorption spectrum taken on a uniform film coated on a quartz glass substrate. The ultraviolet features are no longer obscured by the graphitic carbon background as in our previous spectra²². Broad peaks at 216, 264 and 339 nm dominate the spectra. Weaker structures show up in the visible, including a plateau between ~460 and 500 nm and a small peak near 625 nm. At the bottom of Fig. 5 we have shown positions and relative oscillator strengths taken from Larsson, Volosov and Rosén⁹ calculated for the C₆₀ molecule. They also reported a variety of forbidden bands with the lowest energy ones in the vicinity of 500 nm. There seems to be a rough correspondence between our measurements on solid films and the allowed transitions predicted for the molecule. The possibility exists, however, that one or more of the absorption features shown in Fig. 5 are due to C₇₀. We still do not observe a band at 386 nm in our films, as observed³⁰ using a laser depletion spectroscopy method and attributed to the C₆₀ molecule. Quite similar spectra to that in Fig. 5 have been recorded for microcrystalline coatings deposited at helium pressures of 100 torr, for example. The peaks occur at the slightly shifted positions of 219, 268 and 345 nm.

Possible interstellar dust

The original stimulus for the work² that led to the hypothesis of the soccer-ball-shaped C₆₀ molecule, buckminsterfullerene, was an interest in certain unexplained features in the absorption and emission spectra of interstellar matter. These include an intense absorption band at 217 nm which has long been attributed to small particles of graphite³¹, a group of unidentified interstellar absorption bands in the visible that have defied

explanation for more than 70 years^{31,32}, and several strong emission bands attributed to polycyclic aromatic hydrocarbons^{33,34}. Based on the visible and infrared absorption spectra of Figs 4 and 5, we do not see any obvious matches with the interstellar features. The ultraviolet band at 216–219 nm has a similar peak wavelength to an interstellar feature, although the other strong bands of the spectrum have no interstellar counterparts. As the influence of C₇₀ absorptions on the spectrum is not yet known, a conclusive comparison with the 217-nm interstellar band is difficult. We note that the visible-ultraviolet spectrum presented here is characteristic of a solid, rather than of free molecules. In addition, these new results do not relate directly to absorption in the free C₆₀⁺ molecular ion, which has been envisaged¹⁹ to explain the diffuse interstellar bands. Nevertheless, these data should now provide guidance for possible infrared detection of the C₆₀ molecule, if it is indeed as ubiquitous in the cosmos as some have supposed.

Summary

To our method for producing macroscopic quantities of C₆₀, we have added a method for concentrating it in pure solid form. Analyses including mass spectroscopy, infrared spectroscopy, electron diffraction and X-ray diffraction leave little doubt that we have produced a solid material that apparently has not been reported previously. We call the solid fullerite as a simple extension of the shortened term fullerene, which has been applied to the large cage-shaped molecules typified by buckminsterfullerene (C₆₀). The various physical and chemical properties of C₆₀ can now be measured and speculations concerning its potential uses can be tested. □

Received 7 August; accepted 7 September 1990.

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ACKNOWLEDGEMENTS. W.K. and K.F. thank our colleagues F. Arnold, J. Kissel, O. Möhler, G. Natour, P. Sölter, H. Zscheeg, H. H. Eysel, B. Nuber, W. Kühnbrandt, M. Rentzea and J. Sawatzki. L.D.L. and D.R.H. thank our colleagues J. T. Emmert, D. L. Bentley, W. Bilodeau, K. H. Schramm and D. R. Luffer. D.R.H. thanks the Alexander von Humboldt Stiftung for a senior US Scientist award. We also thank H. W. Kroto and R. F. Curl for discussions.